THE HEATS OF ADSORPTION OF CERTAIN ORGANIC VAPOURS ON CHARCOAL AT 25°

BY

LLOYD McKINLEY

B.A. State University of Iowa, 1919
M.S. State University of Iowa, 1924

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IN
CHEMISTRY

Submitted in Partial Fulfillment of the Requirements for the
DEGREE OF
DOCTOR OF PHILOSOPHY
IN
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BIOGRAPHY

Lloyd McKinley was born at Bridgewater, Iowa, February 4, 1895. He entered the University of Iowa in 1915. At the end of his junior year, he entered the service of the U. S. Army and served until December, 1918. He then returned to the University and received the degree of B.A. in 1919. During the following four years he was instructor in Chemistry and Physics in the High School at Watertown, S. D. He returned to Iowa in 1923 and enrolled in the Department of Chemistry as a graduate assistant and graduate student. He is a member of the honorary and professional societies,—Sigma Xi, Phi Lambda Upsilon, Gamma Alpha, and Phi Delta Chi. He is now head of the department of Chemistry of the Municipal University of Wichita, Kansas.

THE HEATS OF ADSORPTION OF CERTAIN ORGANIC VAPORS ON CHARCOAL AT 25°

BY [illegible] LLOYD McKINLEY

While the adsorptive power of solid porous bodies for gases is a phenomenon that has challenged the attention of many investigators during the last century, the amount of quantitative data which has accumulated dealing with the heat effect accompanying adsorption is rather limited and is confined, for the most part, to the results of comparatively recent investigations. Although the thermal effect of adsorption had been observed by Mitscherlich[1] in 1843, Favre,[2] using a mercury calorimeter, was the first to make a quantitative measurement of the heats of adsorption of a number of gases on charcoal and of hydrogen on platinum. By the use of an ice-calorimeter Chappuis[3] measured the heats of adsorption of sulphur dioxide, ammonia and carbon dioxide on charcoal, meerschaum, platinum black and asbestos. Dewar[4], with the aid of a liquid-air calorimeter, measured the heats of adsorption of the permanent gases on charcoal at the temperature of liquid air. Homfray[5] has shown that a certain thermodynamical formula is applicable for calculating the molecular heat of adsorption of carbon dioxide on charcoal. Using an ice-calorimeter, Titoff[6] obtained consistent values for the thermal effect of adsorption of nitrogen, ammonia and carbon dioxide on charcoal. The heats of adsorption of sulphur dioxide and ammonia on silica gel have been measured by Patrick and Greider.[7] Lamb and Coolidge[8] have obtained values for the heats of adsorption of eleven organic vapors on charcoal. Whitehouse[9] has measured the heat effect produced in the adsorption of carbon dioxide, methane and nitrogen on coals and charcoal. All of these investigators, with the exception of Favre, Homfray and Dewar, have made use of the ice-calorimeter. Beebe and Taylor,[10] and Dew and Taylor,[11] have recently measured the heats of adsorption of hydrogen and ammonia, respectively, on copper and nickel by a rapid method in which the catalyst tube, itself, serves as the calorimeter. They do not, however, claim an accuracy better than 10 percent.

As can be noted from the above review of the literature, the majority of the measurements of the heats of adsorption, thus far, have been made at 0°.

[1] Mitscherlich: Ann. Chim. Phys., (3), **7**, 18 (1843).
[2] Favre: Ann. Chim. Phys., (5) **1**, 209 (1874).
[3] Chappuis: Ann. Chim. Phys., (2) **19**, 21 (1883).
[4] Dewar: Proc. Roy. Soc., **74**, 122 (1904).
[5] Homfray: Z. physik. Chem., **74**, 129 (1910).
[6] Titoff: Z. physik. Chem., **74**, 641 (1910).
[7] Patrick and Greider: J. Phys. Chem., **29**, 1031 (1925).
[8] Lamb and Coolidge: J. Am. Chem. Soc., **42**, 1146 (1920).
[9] Whitehouse: J. Soc. Chem. Ind., **45**, 13 (1926).
[10] Beebe and Taylor: J. Am. Chem. Soc., **26**, 43 (1924).
[11] Dew and Taylor: J. Phys. Chem., **31**, 277 (1927).

Popular as the ice-calorimeter is, it does not permit an investigation at other temperatures. Except for the more difficultly liquefiable gases and vapors, most vapors condense to the liquid state at 0°. This, and the fact that in adsorption there may be a "forced" condensation, does not permit us to separate the thermal effects of the two kinds of condensation. Furthermore, until we are in possession of means of measuring the heat of adsorption at different temperatures, we shall not be able to determine experimentally the effect of temperature upon the heat of adsorption.

The purpose of this investigation was to devise and apply a calorimetric method for measuring the heats of adsorption at any desired temperature. By using higher temperatures we hope later to overcome certain difficulties which arise when working at the temperature of melting ice. Objectionable condensation effects will be avoided, and higher equilibrium pressures can be attained. Although we have not avoided condensation effects by working at 25°, we have, nevertheless, chosen it as our working temperature in this preliminary work. Measurements have been made purposely on some of the vapors studied by Lamb and Coolidge at 0°. In this way we hoped, by comparison, to show the accuracy attainable by the method.

Materials

The charcoal used in this investigation was taken from a large supply which has served as the basis of an extensive study of adsorption in this laboratory. It was prepared for us by the Carbide and Carbon Chemicals Corporation under the direction of Dr. N. K. Chaney. It is a cocoanut shell charcoal which has been activated by steam, treated with acid to remove mineral matter, and then washed until acid-free. The size of the granules used range from 12 to 20 mesh. Previous determinations showed the ash-content to be 0.28 percent by weight.

The loss in weight on outgassing and the density of the charcoal have been determined in an earlier work.[12] For the former, a weighed sample of the charcoal was evacuated under identical conditions employed in the regular adsorption experiments. When the pressure had remained constant at about 0.0001 mm. for several hours the tube was sealed off and weighed. The mean of three very concordant determinations showed a 2.50 percent loss in weight on outgassing; this correction was applied in calculating the actual weight of the adsorbent used. The density of the charcoal was determined by the method of Cude and Hulett,[13] using water as the immersion liquid and disregarding the drift after the first few hours. The mean of four determinations, 1.800, was taken as the density and was used in correcting for the "dead space."

The liquids, whose vapors were studied, were purified carefully by accepted methods,[14] and then fractionated. Only the middle portion of each fractionation was collected. These liquids were prepared immediately before using.

[12] Pearce and Knudson: Proc. Iowa Acad. Sciences, (1927).
[13] Cude and Hulett: J. Am. Chem. Soc., 42, 391 (1920).
[14] Mathews: J. Am. Chem. Soc., 48, 562 (1926).

Apparatus

The apparatus is shown in Figs. 1 and 1a. It combines the advantages of recently improved adsorption apparatus with those of a calorimeter which may be used at any temperature. The net result is an apparatus more potential in possibilities than any hitherto used in measuring the heats of adsorption.

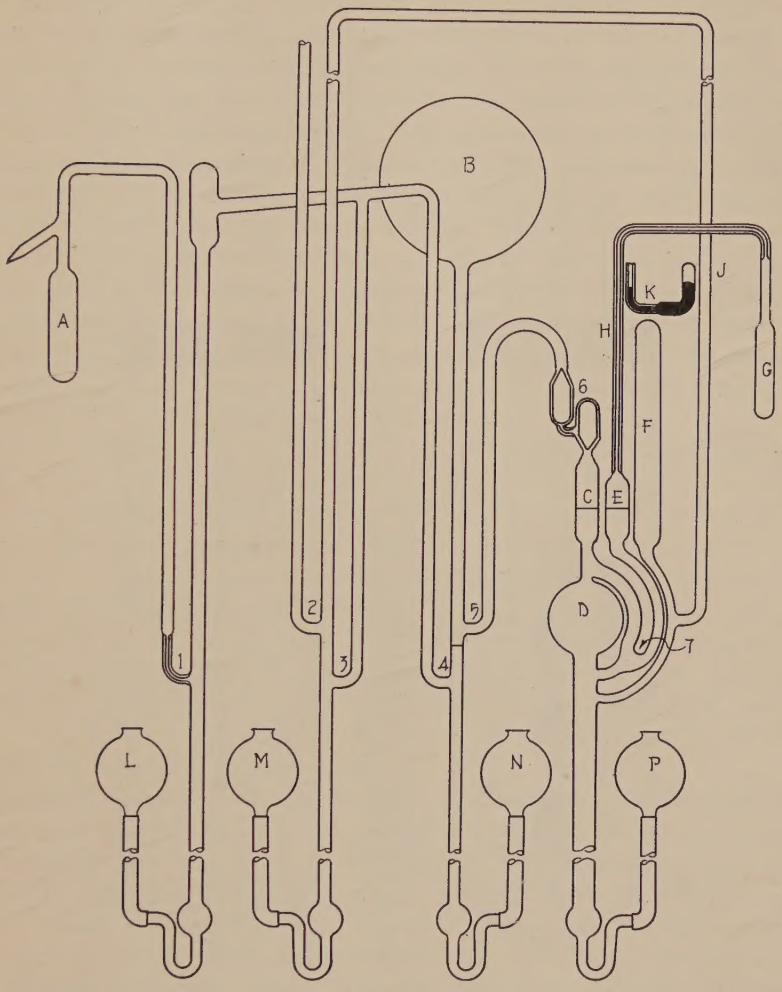

FIG. 1

Adsorption Apparatus.—The adsorption apparatus consists of one continuous line of Pyrex tubing and flasks, with no stopcocks or rubber connections above the mercury levels; it is, essentially, in design and principle, the same as that used by Coolidge.[15] For the sake of brevity, a detailed explanation

[15] Coolidge: J. Am. Chem. Soc., **46**, 596 (1924).

of the various parts is omitted. A detailed description of the apparatus and its operation is given in the original paper.

Calorimeter.—The calorimeter, R, is a wide-mouth Dewar flask, fitted with a cork stopper with openings for the charcoal bulb, G, the spiral rotary stirrer, P, one arm of the thermocouple, Q, and a special low lag heating coil, N.

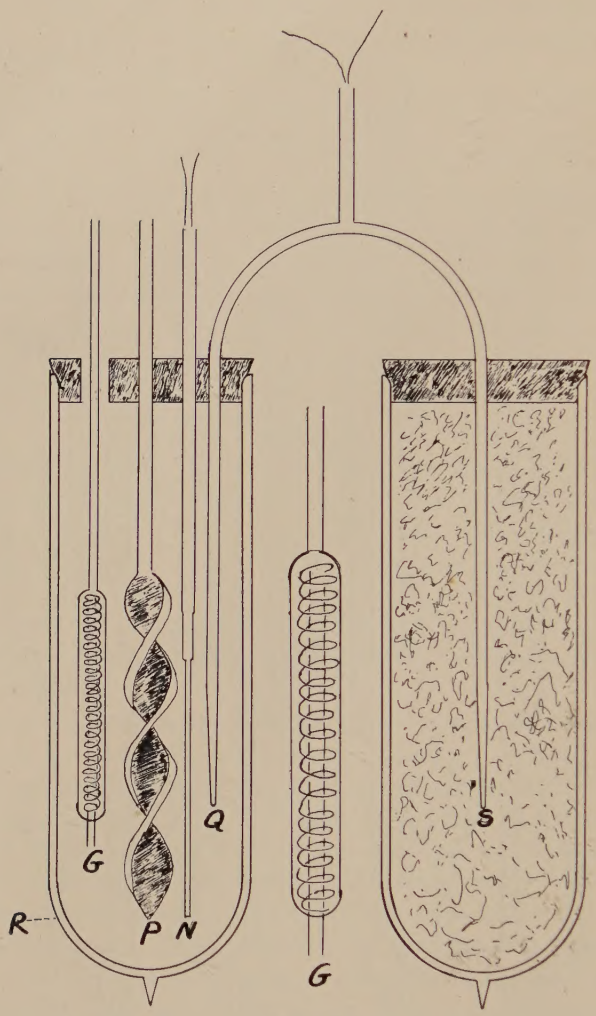

FIG. 1a

The charcoal bulb of "702 P" Pyrex glass, Fig. 1a, G, contains a spiral and a straight piece of tungsten wire, both sealed into the bottom of the bulb so that about 2 cms. protrude. The wires within the bulb are so arranged that the distance between the adjacent wires does not exceed 3 mm. In this way the heat liberated in the adsorption process is quickly conducted from the charcoal surface to the calorimeter liquid.

Constant Temperature Bath.—The complete apparatus with the exception of the bulb, A, is inclosed in a double-walled, electrically heated and electrically controlled air-bath mounted on a heavy table. Efficient stirring is obtained by a system of high-speed fans which maintain a continuous and rapid circulation of air through the bath, over the cooling coils at the top, then down between the walls at the sides, and finally past the low lag heating coils into the bottom of the bath. This efficient circulation of the air, together with a 5-foot upright multiple-tube mercury regulator in series with a Bunnel relay, enabled us to control the temperature of the bath to within $\pm 0.05°$. At the front and back are large double doors which provide, not only a non-conducting air space, but also a ready means of accessibility to the apparatus when in need of alteration or repairs. The glass doors at the front permitted readings of the bath temperature and of the vapor pressures by means of a cathetometer placed outside. Ideal working conditions were realized by means of a special precision system of mercury controlling devices operated from a panel of convenient switches on the front of the table.

The volume of the reservoir, B, together with the connecting tube to the mark between valves 4 and 5, and thence to the mark on C, was determined from its water capacity before the apparatus was assembled. The volume of the charcoal bulb, G, plus the capillary tube to the mark on E, was likewise calibrated with mercury before assembling.

Thermo-element.—The 25-junction copper-constantan thermo-element was made in strict accord with the specifications given by White.[16] The element was accurately standardized against a certified thermo-element at three points, namely, the transition points of $Na_2SO_4.10H_2O$ and $MnCl_2.2H_2O$, and liquid air. The salts were carefully purified according to the methods of Richards and Wrede,[17] and of Richards and Wells,[18], respectively. The reference ice bath consisted of a large Dewar flask containing pure ice moistened with conductivity water. Since the thermal measurements made in this work were at 25°, we have calculated the potentials corresponding to 25° and 26°. They were found to be 22856μv and 23802μv, respectively; the difference corresponds to 0.0010559° per 1 μv.

Thermal Capacity of the Calorimeter.—The calibration of the calorimeter system with water as the calorimeter liquid was made electrically by passing an accurately known quantity of electricity through a heating coil of known resistance. This coil consisted of about 100 cms. of No. 36 constantan wire wound around a thin mica strip. It was insulated by two similar strips of mica and inclosed in a close fitting copper case. Two heavy insulated copper leads pass from the case, proper, through a short metal tube that is cemented to a glass tube, which serves as a handle and as a heat insulator. The metallic parts of the receptacle, which is made air tight by soldering, is heavily plated with silver and polished. The resistance is 52 ohms, and in operation delivers about 3 watts.

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[16] White, J. Am. Chem. Soc., **36**, 2292 (1914).
[17] Richards and Wrede, Z. physik. Chem., **61**, 313 (1907).
[18] Richards and Wells, Z. physik. Chem., **43**, 465 (1903).

Method of Calibration.—The heating coil was connected in series with a standard 1-ohm resistance, a laboratory slide rheostat and a very sensitive Bradleystat. A battery of seven large storage cells supplied the current. Across the standard ohm and the heating element were connected a Leeds and Northrup, "Type K," potentiometer and a volt-box, respectively. With this arrangement, the potentiometer reads directly in amperes, whereas the volt-box in conjunction with a student potentiometer permits the reading of the volts. With the potentiometer set to read the amount of current chosen to flow through the system, the rheostat was adjusted so that a slight manipulation of the Bradleystat enables the operator to maintain a current whose variations at any instant never exceed 1 part in 1000. A sensitive galvanometer indicated the deviations which can be instantly corrected. The voltage drop across the heating coil was read at intervals of one minute, and was found to be practically constant. When the voltage did actually vary, the average value during the interval was calculated and used. The time of passage of the current was measured by means of a stop watch, reading to 0.2 sec.

The increase in temperature during a calibration, although small, corresponded to an increment of approximately 2000 μv. Since the galvanometer was responsive to deviations of 1 μv., the possible error in this measurement was not greater than 0.1 percent. Radiation, though perceptible, was measurable. The magnitude of the radiation was greatly reduced by starting the calibration at a calorimeter temperature that was as far below, as the final temperature was above, that of the constant temperature bath.

The results of two determinations of the thermal capacity of the calorimeter and its fixtures were 51.26 cals. and 51.42 cals., with a deviation from the mean, 51.34 cals., of less than 0.2 percent. The value of 51.34 cals. was accordingly accepted as the thermal capacity of the calorimeter and was used in all subsequent calculations.

Specific Heat of "Finol."—Following the same procedure as outlined for water, we obtained the thermal capacity of the calorimeter system and liquid when charged with an accurately known weight of a light oil, which is sold under the trade name of "Finol." With 300 cc. of this oil in the calorimeter, the total heat capacity is only about 165 cals., an amount which is less than one-half that with an equal volume of water as the liquid. Three different determinations of the specific heat of the oil, in calories, over the range from 25° to 28°, gave the values 0.4500, 0.4492 and 0.4512, respectively, or a mean specific heat of 0.4501 cals.

Sensitivity of Calorimeter

The thermal capacity of the calorimeter and liquid is equal to the thermal capacity of the calorimeter, (51.34), plus the product of the weight of the oil times its specific heat, 0.4501 cals. For the average weight of oil used, this amounts to 165 cals. Since the thermo-couple used was sensitive to 0.001°, the calorimeter system responds to a heat transfer of 0.17 cal. In using the ice calorimeter for their measurements, Lamb and Coolidge state that on their

scale a millimeter movement of the mercury thread, during the change of state from ice to water, corresponds to 0.589 cal. Hence the resulting sensitivity of the ice calorimeter is three times that of our calorimeter, if the displacement of the mercury thread can be read to 0.1 mm. The results of our work show, however, that this difference in sensitivity is not appreciable.

Experimental Method

The charcoal bulb, first weighed empty and then full of charcoal, is sealed into position, inclosed in an electric furnace at 550°, and evacuated until the McLeod gage, (not shown in Fig.), indicates a pressure of 0.0001 mm., or less. All of the mercury levels are lowered so that the whole system is evacuated at the same time. Mercury well, L, is now raised, closing valve 1, the pumping is discontinued and the furnace is allowed to cool. The procedure involved in charging A with liquid and B with vapor, as well as that involved in transferring the vapor to the charcoal, if not evident to the reader, can be found in the paper by Coolidge,[15] who worked with a similar apparatus. An additional feature is a reservoir used when the transfer of large volumes of vapor is required to produce high equilibrium pressures. This consists of a mercury well and bulb (not shown), but attached to the capillary, H.

The calorimeter is charged with a weighed amount of oil, initially at or very near the temperature of the bath, and is allowed to stand with intermittent stirring until a constant reading of the thermo-element is obtained. When thermal equilibrium is attained and the cathetometer pressure readings become constant, a sample of the vapor is transferred to the charcoal by means of the pump, D. After the admission of the vapor to the charcoal, the liquid is stirred intermittently for periods of one to three minutes. During this time the thermo-element potentials are read at one minute intervals until the potential attains a constant value, or until a constant rate of radiation is indicated. Pressure readings are then taken of the vapor remaining in the reservoir, and of the vapor in equilibrium with the charcoal. Once the equilibrium is established and the data recorded, a new sample of vapor is admitted. With each admission of vapor, there are recorded the potential increments in microvolts, the corresponding drop in the presence of the vapor in B, and the successively increasing equilibrium pressures over the charcoal. When the equilibrium pressure has attained a value just short of that at saturation a series of adsorption experiments, or "run," is assumed to be completed.

Calculation of Results

The results are expressed in small calories and cc. of gas (N.T.P.) per gram of gas-free charcoal. The vapor pressures were corrected for altitude and temperature, and the gas laws were applied in calculating the volume of the vapor. The complete calculations of an experiment are given below.

Weight of charcoal and glass bulb	28.6705 g.
Weight of bulb	25.5844 g.
Weight of charcoal	3.0861 g.

Corrected weight of charcoal[13]	3.0089 g.
Volume of total reservoir system (N.T.P.)	2203.6 cc.
Pressure in B before adsorption	9.775 cm.
Pressure in B after adsorption	8.755 cm.
Drop in pressure	1.020 cm.
Correction for temperature and altitude	0.005 cm.
Corrected pressure drop in B	1.015 cm.
Gas removed (per g. of char.) for 1 cm. drop in pressure:	

$$\frac{2203.6 \times 273}{76 \times 298 \times 3.0089} = 8.828 \text{ cc.}$$

For 1.015 cm. drop the cc./g. removed is	8.96 cc.
Pressure in charcoal bulb at equilibrium	0.00 cm.
Volume of bulb and tubing to calibration marks	14.900 cc.
Volume of charcoal: 3.0089 + 1.800	1.671 cc.
Volume of "dead space"	12.229 cc.

$$\frac{13.229 \times 273}{76 \times 298 \times 3.0089} = 0.053 \text{ cc./g.}$$

Gas removed but not adsorbed	0.00 cc./g.
Gas adsorbed "x"	8.96 cc./g.
Initial reading of thermocouple at 7.46 P.M.	22874 μv.
Time required to introduce vapor: 7.46 to 7.52	6 min.

Stirrer started at 7.52 (60 R.P.M.)

Time	Thermocouple reading
7.54	22941 μv.
7.55	22958 μv.
7.56	22965 μv.
Rate of stirring decreased (30 R.P.M.)	
7.57	22970 μv.
7.58	22975 μv.
Stirrer stopped.	
8.00	22979 μv.
(At this time pressure readings were taken)	
8.13	22996 μv.
Stirrer operated 1 min.	
8.15	22990 μv.
8.16	22990 μv.
8.19	22990 μv.

Final reading of the thermocouple	22990 μv.
Increase in microvolts	116 μv.
Weight of oil in calorimeter	252.66 g.

Cal./g. evolved corresponding to increase of 1 μv:

$$\frac{(252.66 \times 0.4501) - 51.34}{947 \times 3.0089} = 0.057927 \text{ cal./g./1 } \mu\text{v.}$$

Total heat evolved per gram of charcoal, "h": $116 \times 0.057927 = 6.72$ cal./g.

The results of each experiment, namely, the drop in pressure and the heat evolved are added to those of the preceding experiments of the same run, thus giving the total heat evolved, h, and the total drop in pressure in B, during the adsorption of the vapor. This change in pressure enables us to calculate the total gas volume, x, adsorbed by the charcoal.

Results

The results of the study of the heats of adsorption of nine vapors on charcoal are recorded in the following Tables. The first column in each gives the equilibrium pressure observed at the time when the final calorimeter reading

TABLE I

The Heat of Adsorption of Acetone Vapor at Charcoal at 25°

P cm.	X cc./g	ΔE μv.	Δh cal./g.	Σh cal./g.	Σh cal./g.	Δ cal./g.
———	6.44	77	4.59	4.59	4.55	−0.04
———	15.90	111	6.62	11.21	10.78	−0.63
———	29.45	137	8.15	19.36	19.40	+0.04
0.110	47.93	194	11.53	30.89	30.87	−0.02
0.245	64.76	202	12.01	42.90	41.13	−0.77
4.085	99.87	330	19.62	62.52	62.21	−0.30
13.024	109.28	90	5.35	67.87	67.72	−0.15

Fresh sample. $h = 0.7713\, x^{0.9534}$

TABLE II

The Heat of Adsorption of Ether Vapor at Charcoal at 25°

P cm.	X cc./g.	ΔE μv.	Δh cal./g.	Σh_o cal./g.	Σh_c cal./g.	Δ cal./g.
———	11.72	155	9.14	9.14	9.25	+0.11
———	28.39	197	11.61	20.75	20.67	−0.08
———	45.89	209	12.32	33.07	32.40	−0.67
1.365	65.83	210	12.34	45.41	45.41	0.00
35.020	70.72	108	6.35	51.76	53.68	(+1.92)
———	8.39	108	6.36	6.36	6.61	+0.25
———	24.26	193	11.49	17.85	17.85	0.00
———	39.81	186	10.96	28.81	28.37	−0.44
———	55.36	161	9.48	38.29	38.62	+0.33
4.185	66.99	143	8.42	46.71	47.44	+0.73
36.718	78.00	61	3.59	50.30	53.22	(+2.92)

Used previously on acetone. $h = 0.9044\, x^{0.0353}$

TABLE III

The Heat of Adsorption of Carbon Disulphide Vapor by Charcoal at 25°

P cm.	X cc./g.	ΔE μv.	Δh cal./g.	Σh_o cal./g.	Σh_c cal./g.	Δ cal./g.
———	3.73	50	2.98	2.94	2.61	−0.33
———	18.81	150	8.93	11.78	11.38	−0.40
———	32.84	131	7.80	19.49	18.92	−0.57
———	46.43	117	6.97	26.33	25.94	−0.39
0.475	59.57	102	6.07	32.39	32.55	+0.16
0.860	77.52	147	8.73	41.04	41.35	+0.31
5.952	114.83	324	19.29	60.13	59.18	−0.95
———	7.50	82	4.82	4.82	4.93	+0.11
———	20.56	128	7.53	12.35	12.35	0.00
———	31.78	99	5.82	18.17	18.36	+0.19
———	42.27	84	4.94	23.11	23.81	+0.70
———	62.70	179	10.53	33.64	34.10	+0.46
0.630	84.29	183	10.77	44.41	44.65	+0.24
1.742	106.08	181	10.65	55.06	55.06	0.00
21.145	130.45	184	10.82	65.88	66.47	+0.59
———	11.67	123	7.24	7.24	7.37	+0.13
———	30.56	187	11.01	18.25	17.72	−0.53
———	55.90	221	13.02	31.27	30.71	−0.56
———	81.28	204	12.02	43.39	43.19	−0.20
1.135	102.75	174	10.25	53.54	53.48	−0.06
20.006	128.27	189	11.13	64.67	65.46	−0.79

Use previously in Expts. I and II. $h = 0.7861\, x^{0.911}$

TABLE IV

The Heat of Adsorption of Benzene Vapor by Charcoal at 25°

P cm.	X cc./g.	ΔE μv.	Δh cal./g.	Σh_o cal./g.	Σh_c cal./g.	Δ cal./g.
———	14.00	181	10.67	10.67	10.34	−0.33
———	27.30	152	8.96	19.63	19.60	−0.03
———	46.52	215	12.67	32.30	32.64	+0.34
———	66.39	217	12.79	45.09	45.87	+0.78
———	79.22	134	7.90	52.99	54.32	+1.38
6.065	87.29	85	5.01	58.00	59.61	+1.61
———	12.39	153	9.00	9.00	9.23	+0.23
———	20.55	109	6.41	15.41	14.93	−0.48
———	47.72	310	18.24	33.65	33.44	−0.21
———	59.43	138	8.12	41.77	41.26	−0.51
———	71.54	127	7.47	49.24	49.28	+0.04
2.000	80.72	100	5.88	55.12	55.30	+0.18
5.798	85.39	62	3.65	58.77		

$h = 0.828\, x^{0.9569}$

Used previously in expts. I, II and III.

was made. The second column gives the volume of gas in cc. (N.T.P.) adsorbed by 1 g. of gas-free charcoal. In the third are placed the increase in the thermocouple reading, in μv, accompanying the transfer of the vapor. These readings, converted to calories, Δh, are listed in the fourth column. The fifth contains the summation, Σh, of the heat effects of the previous additions of the same series. In the sixth are placed the values of Σh calculated by means of the exponential formula, placed at the bottom of the table. The previous history of the sample is also given below the results for each liquid.

TABLE V

The Heat of Adsorption of Ethyl Chloride Vapor by Charcoal at 25°

P cm.	X cc./.g.	ΔE μv.	Δh cal./g.	Σh_o cal./g.	Σh_c cal./g.	Δ cal./g.
———	7.00	65	3.82	3.82	3.61	−0.21
———	23.37	147	8.65	12.47	12.46	−0.01
———	40.39	142	8.35	20.52	21.68	+0.68
1.455	63.78	187	11.00	31.82	33.00	+1.18
4.300	81.80	150	8.82	40.64	42.01	+1.33
22.345	99.49	172	10.12	50.76	50.80	+0.04
———	8.13	70	4.13	4.13	4.75	+0.62
———	18.09	100	5.90	10.03	9.72	+0.31
———	27.12	70	4.13	14.16	14.40	+0.24
———	43.97	175	10.33	24.49	23.00	−1.49
1.820	62.67	138	8.14	32.63	32.59	−0.04
5.569	82.09	164	9.68	42.31	42.15	−0.16

$h = 0.5862\, x^{0.9700}$

Used previoulsy in expts. I, II, III and IV.

TABLE VI

The Heat of Adsorption of Methyl Alcohol Vapor by Charcoal at 25°

P cm.	X cc./g.	ΔE μv.	Δh cal./g.	Σh_o cal./g.	Σh_c cal./g.	Δ cal./g.
———	15.32	180	10.43	10.43	10.49	+0.06
———	29.74	155	8.98	19.41	19.20	−0.21
———	44.11	139	8.05	27.46	27.50	+0.04
———	63.75	191	11.06	38.52	38.46	−0.06
0.840	85.50	198	11.47	49.99	50.26	+0.27
———	8.96	116	6.72	6.72	6.44	−0.28
———	23.42	150	8.69	15.41	15.45	+0.04
———	33.13	85	4.98	20.39	21.19	+0.80
———	48.41	144	8.34	28.73	29.93	+1.20
0.485	74.65	254	14.71	43.44	44.42	+0.98
0.725	98.80	217	12.57	56.01	57.33	+1.32
1.430	126.41	302	17.46	73.47	71.77	−1.70
4.135	158.03	253	14.62	88.09	87.96	−0.13

Fresh sample. $h = 0.873\, x^{0.9111}$

TABLE VII

The Heat of Adsorption of Chloroform by Charcoal at 25°

P cm.	X cc./g.	ΔE μv.	Δh cal./g.	Σh_o cal./g.	Σh_c cal./g.	Δ cal./g.
———	9.40	117	6.76	6.76	6.74	−0.02
———	20.83	133	7.69	14.45	14.18	−0.27
———	34.84	152	8.79	23.24	22.94	−0.30
———	56.41	218	12.60	35.84	36.00	+0.16
0.465	74.80	186	10.75	46.59	46.87	+0.28
12.382	94.45	175	10.12	56.71	58.30	+1.59
———	12.40	151	8.73	8.73	8.73	0.00
———	31.63	219	12.66	21.39	20.96	−0.43
———	47.63	161	9.31	30.70	30.73	+0.03
———	67.30	193	11.16	41.86	42.37	+0.51
2.702	81.23	141	8.15	50.01	50.63	+0.62
13.188	90.82	41	4.97	54.98	56.20	+1.23

Previously used with methyl alcohol. $h = 0.8295\ x^{0.935}$

TABLE VIII

The Heat of Adsorption of Carbon Tetrachloride Vapor by Charcoal at 25°

P cm.	X cc./g.	ΔE μv.	Δh cal./g.	Σh_o cal./g.	Σh_c cal./g.	Δ cal./g.
———	9.44	136	7.88	7.88	7.76	−0.12
———	21.58	148	8.57	16.45	16.41	−0.04
———	32.95	128	7.41	23.86	23.80	−0.06
———	42.35	104	6.02	29.88	29.67	−0.21
5.982	53.23	117	6.78	36.66	36.27	−0.39
9.496	57.67	41	2.37	39.03	38.91	+0.12
———	3.44	55	3.18	3.18	3.27	+0.09
———	11.07	100	5.79	8.97	9.11	+0.14
———	18.63	89	5.15	14.12	14.43	+0.31
0.215	28.11	99	5.73	19.85	20.70	+0.85
0.285	36.18	98	5.67	25.52	25.84	+0.32
5.425	47.59	115	6.65	32.17	32.87	+0.70

Used in expts. VI and VII. $h = 1.107\ x^{0.878}$.

TABLE IX

The Heat of Adsorption of Propyl Chloride Vapor by Charcoal at 25°

P cm.	X cc./g.	ΔE μv.	Δh cal./g.	Σh_o cal./g.	Σh_c cal./g.	Δ cal./g.
———	8.39	112	6.48	6.48	6.56	+0.08
———	24.65	188	10.88	17.36	17.52	+0.16
0.190	37.99	151	8.74	26.10	25.99	−0.11
0.590	54.54	180	10.41	36.51	36.15	−0.36
5.509	66.10	115	6.65	43.16	43.06	−0.10
34.954	77.98	98	5.67	48.83	50.07	+1.24

Used in expts. VI, VII and VIII. $h = 0.9441\ x^{0.9915}$.

If the observed values of X and h are plotted, we obtain curves which are slightly concave toward the X-axis. Fig. 2 shows the curves for all of the vapors drawn from a common origin. In order to prevent overlapping, a plot is made in which the origin is displaced one square with respect to the

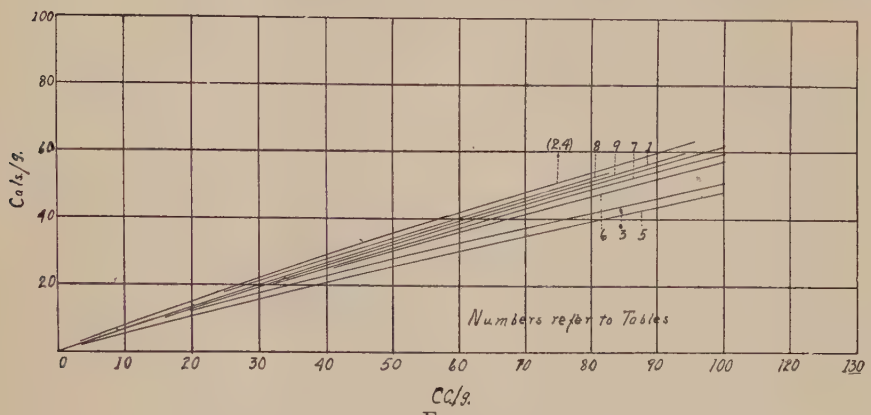

Fig. 2

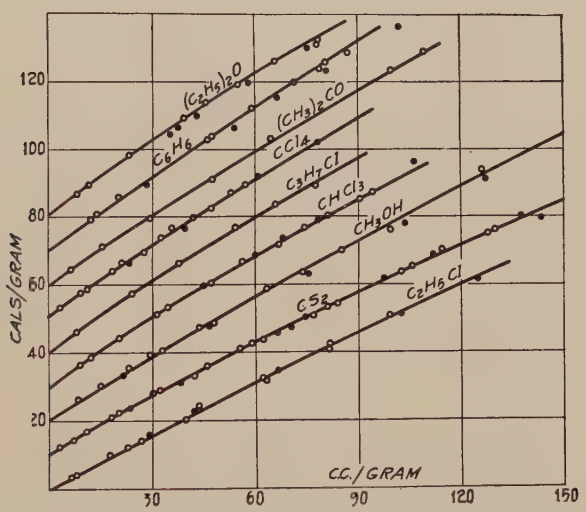

Fig. 3

next one to it, giving the system of curves in Fig. 3. The data obtained by Lamb and Coolidge at 0° are also indicated by the points, x. When the values of log n are plotted against the corresponding values of log x, we get the curves in Fig. 4, from which the experimental values show slight, if any, deviations. From the position and slopes of these lines, (Fig. 5), we obtain the constants of the equation:

$$\log h = \log m - n \log X, \text{ or } h = m X^n.$$

The constants obtained in this way have been used to calculate the values of h which are given in the sixth column of each Table. In the seventh col-

umn are placed the differences, △, between the observed and calculated values. In case that more than one series of experiments was made with the same vapor, the same sample of charcoal was used. The fact that all of the points fall almost exactly upon the curve shows that the vapor is without influence upon the adsorption power of the charcoal.

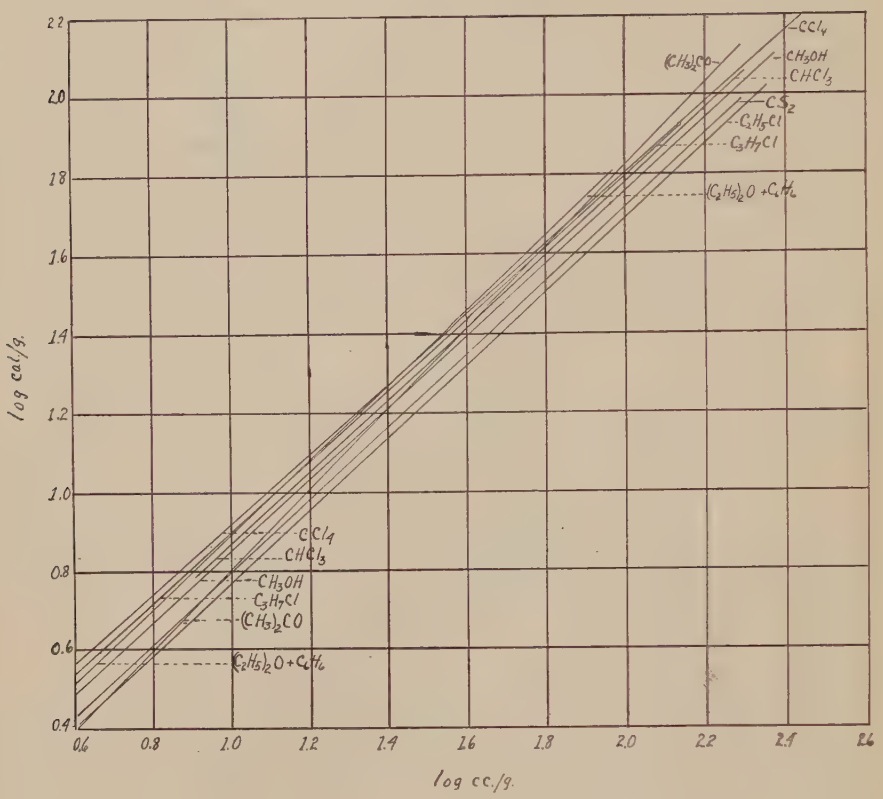

FIG. 4

Reproducibility and Reliability of Results

The results presented in Tables I to IX, and in Figs. 2 to 5, have been obtained with various weights of charcoal, some fresh, others previously used, and with variations in time and quantity of vapor admitted to the charcoal. The agreement between data on a fresh sample and on one which has been used is excellent. The agreement between duplicate runs for a given liquid is as good as that between the individual experiments. This is shown by Figs. 3 to 6. At most, the deviations are very slight. In general, the data of Lamb and Coolidge, indicated by points, x, are seen to be in close agreement.

These observations indicate that the total quantity of heat evolved during adsorption by gas-free charcoal is definite and reproducible. It is not affected by the manner in which the vapor is added, whether it is added slowly or rapidly, all at once, or in small portions. It is independent of the previous

history of the charcoal, provided the charcoal is previously evacuated at 550°. The calorimeter reading usually indicated adsorption equilibrium within eight to twenty minutes, and no appreciable "creeping" was ever observed. Vapors, such as carbon tetrachloride and chloroform, which are known to

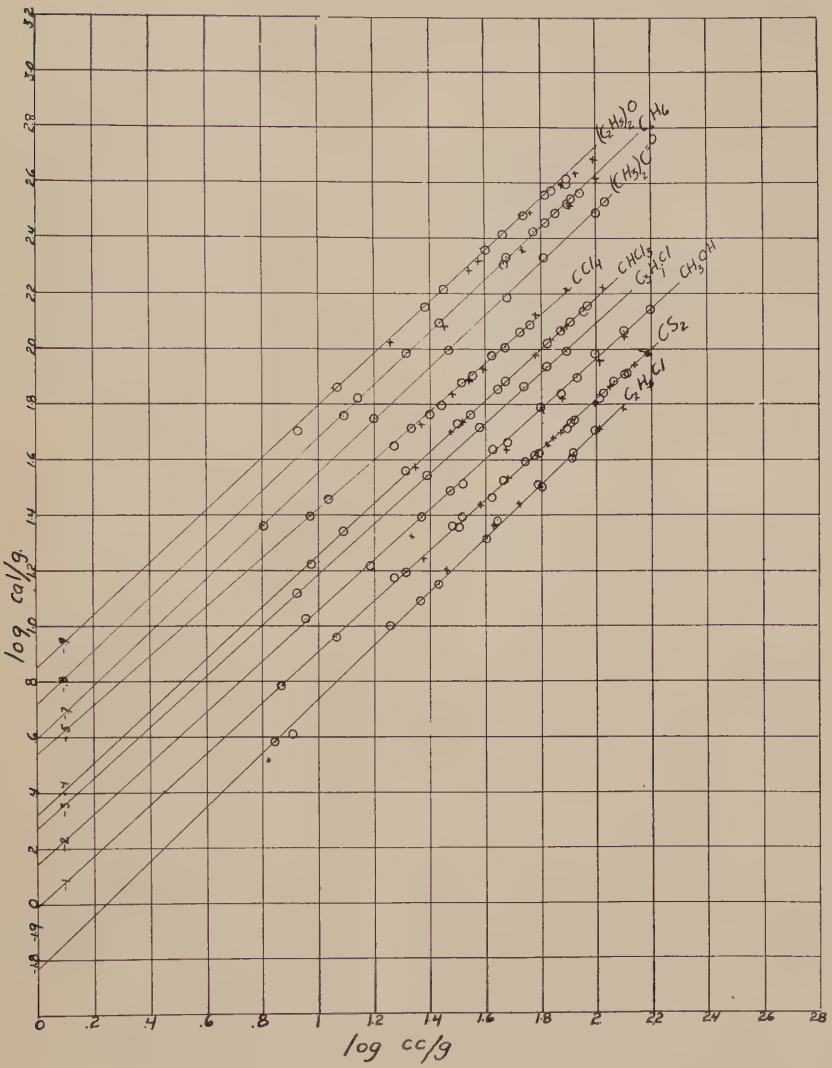

FIG. 5

poison charcoal, do not appear to reduce appreciably the quantity of heat evolved when a given volume of vapor is adsorbed in a subsequent run on the same sample. This is contrary to the observation of Lamb and Coolidge, who report that vapors studied with poisoned samples of charcoal give values for the heat evolved which are about 10 percent lower than with fresh samples.

Discussion of Results

In attempting to calculate the molecular heat of adsorption, h_m, from the data, we might simply solve for h in the equations,

$$h = mX^n,$$

after substituting for X, the volume of a gram molecule of the vapor, 22410 cc., and making use of the characteristic constants, m and n, obtained from the logarithmic plot. The resulting value for h, which would be the molecular heat of adsorption per one gram of charcoal, is impossible from a practical standpoint. In arriving at their values for h_m, Lamb and Coolidge chose to express it as the heat evolved when one mol of vapor is adsorbed by 500 g. of charcoal. This choice follows directly and conveniently from the fact that 1/500 mol of vapor is equivalent, in cc., to the average mid-point of the range of volume of vapor adsorbed by one gram of their charcoal. This mid-point they designate as 44.6 cc. In order the better to compare the results obtained by the two methods, we have made our calculations on the same basis as that used by Lamb and Coolidge. The results obtained by both methods are given in Table X. In making this comparison we must bear in mind that we have no knowledge of the mineral content of the charcoal which they have used.

TABLE X

Summary of Calorimetric Results on "Acid Washed," "Ash Free" Charcoal at 25°

Vapor	Mol. Vol. Liq. 25° cc.	n 25° Expt.	n 0° L-C	m 25° Expt.	m 0° L-C	h_m. 25° Expt. K-cal.	h_m. 0° L-C K-cal.
C_2H_5Cl	71.1*	0.9700	0.9150	0.5862	0.7385	11.5	12.0
CS_2	60.7	0.9110	0.9205	0.7861	0.7525	12.5	12.5
CH_3OH	40.7	0.9111	0.9380	0.8730	0.7420	13.9	13.1
$(CH_3)_2CO$	73.9	0.9534	———	0.7713	———	14.4	———
$CHCl_3$	80.7	0.9350	0.9350	0.8295	0.8295	14.5	14.5
C_3H_7Cl	89.0	0.9115	———	0.9441	———	15.4	———
CCl_4	97.1	0.8780	0.9300	1.1070	0.8930	15.4	15.3
C_6H_6	89.4	0.9569	0.9590	0.828	0.774	15.7	14.7
$(C_2H_5)_2O$	104.7	0.9353	0.9215	0.9044	0.9170	15.8	15.5

*Estimated.

Since the ground covered in this work is practically the same as that covered by Lamb and Coolidge, we can, in the discussion of these results, as well as of those that follow, do little more than make a comparison of the results obtained at the two temperatures by two entirely different methods. Perhaps the most striking relation to be observed in Table X is that for the calculated values of the molecular heats of adsorption, h_m. Except for ethyl chloride, methyl alcohol and benzene, the values are almost, if not identical. The molecular volume of ethyl chloride at 25° had to be estimated, and, hence, calculations depending upon it should have little weight. Omitting ethyl

chloride and carbon bisulphide, the values of h_m calculated for 25° do increase with increase in the molecular volume of the liquid. It will be observed also that the value of n is always less than unity. Even including the value of n for benzene, the maximum deviation from the mean value, 0.918, is only 5.6 percent. The values of m vary much more widely than do those of n, and, furthermore, there is a decided tendency for m to be small when n is large. Except for chloroform, the values of these constants seem to be dependent upon the temperature. In general, as the value of m increases with the temperature that of n decreases. The reverse relation is equally true. Lamb and Coolidge[8] have shown by a graph that there is a decided relation between the values of $1-n$ and the boiling points of the liquids. They state that this parallelism indicates that the higher the boiling point of the liquid, the less marked is the "fatigue." No parallelism between n or m and any physical property of the liquids is directly apparent from our data.

No final conclusion as to the effect of temperature upon the molecular heat of adsorption can be drawn from the comparison of the data obtained at 0° and 25°. It suffices to say that the effect of temperature, in general, is not marked.

From a theoretical standpoint, the views regarding the effect of temperature upon the heat of adsorption are conflicting. In the first place, according to Lorentz and Lande,[19] but in opposition to the views of Eucken,[20] the adsorption potential, which is really the heat of adsorption, should, in general, vary with the temperature. Secondly, it can be shown that the isosteres, obtained by plotting the values of the log p against the reciprocal of the absolute temperature, are in general for any one vapor linear and parallel, and, therefore, are of the same slope. If the value of $Rd \ln p/d(1/T)$ does not vary with the temperature, we should expect the heat of adsorption to be independent of the temperature and concentration. One objection to the use of the isosteres as a means of calculating the heat of adsorption is the fact that the values thus calculated are often too low and they do not include that appreciable part of the range of adsorption where p is too small to be measured accurately.

Lamb and Coolidge[8] maintain that the process of adsorption may be considered as taking place in two steps: first, a compression of the vapor to such a point that liquefaction ensues, and second, a further compression of this liquid by the attractive forces of the adsorbent. The observed heat of adsorption will then be made up of two quantities, the heat of vaporization of the liquid, and that which may be designated as the *net* heat of adsorption. The latter quantity they showed to be proportional to the heat of compression of the liquid under high pressure. In accordance with this theory, the effect of temperature upon the heat of adsorption will be the result of two effects: one upon the heat of vaporization, and the other upon the heat of compression.

The molecular heats of adsorption of each of the nine vapors have been calculated for 25°. They are included with related data in Table XI. The

[19] Lorentz and Lande: Z. anorg. Chem., **125**, 47 (1922).
[20] Eucken: Ber., **12**, 45 (1914).

second column contains the values for the molecular heats of adsorption when 1 cc. of liquid is adsorbed by 10 g. of charcoal; column 3 contains the molecular heats of vaporization, and column 4 the net heats of adsorption.

TABLE XI

Relation between Heats of Adsorption and Heats of Compression at 25°

1	2	3	4	5	6	7	8	9
	h	Q	h−Q	h−Q	$\frac{dQ}{dP}$	$\frac{\text{col. 5}}{\text{col. 6}}$	$\frac{dQ}{dP}$	$\frac{\text{col. 5}}{\text{col. 8}}$
Vapor	K. cal.	K. cal.	K. cal.	1 cc. K. cal.	1 cc. cal.	x 1000 at.	1 cc. cal.	x 100 at.
C_2H_5Cl	11.85	5.96*	5.88	0.0828	0.01210	6.8	0.00351	23.6
CS_2	12.77	6.45	6.32	0.1041	0.00865	12.0	0.00343	30.8
CH_3OH	13.69	8.95	4.74	0.1165	0.00893	13.0	0.00351	35.0
$(CH_3)_2CO$	14.74	7.66	7.08	0.0958	0.01050	9.1	0.00383	25.1
$CHCl_3$	14.97	7.72	7.25	0.0896	0.00914	9.8	———	———
C_3H_7Cl	15.90	6.90†	9.00	0.1011	0.00837	12.1	———	———
CCl_4	16.90	7.72	9.18	0.0945	0.01260	7.5	———	———
C_6H_6	16.14	8.03	8.11	0.0907	0.00872	10.4	———	———
$(C_2H_5)_2O$	16.62	6.44	10.18	0.0972	0.01186	8.2	0.00316	30.4
Average				0.0969	0.0101	10.3	0.00350	29.0

*Mol. vol. estimated.
†Calculated from vapor pressure data.

TABLE XII

Relation between Heats of Adsorption and Heats of Compression at 0°

1	2	3	4	5	6	7	8	9
	h.	Q.	h-Q	h-Q	$\frac{dQ}{dP}$	$\frac{\text{col. 5}}{\text{col. 6}}$	$\frac{dQ}{dP}$	$\frac{\text{col. 5}}{\text{col. 8}}$
Vapor	K. cal.	K. cal.	K. cal.	K. cal.	1 cc.	x 1000 at.	1 cc.	x 1000 at.
C_2H_5Cl	12.33	6.22[a]	6.11	0.0864	0.0101	8.5	0.00314	27.5
CS_2	12.63	6.83	5.80	0.0991	0.0073	13.5	0.00326	30.2
CH_3OH	12.95	9.33	3.62	0.0908	0.0076	12.0	0.00312	28.9
C_2H_5Br	14.33	6.85[a]	7.48	0.1020	0.0086	11.9	0.00349	29.2
C_2H_5I	14.25	7.81[a]	6.44	0.0815	0.0074	11.0	0.00312	26.1
$CHCl_3$	14.93	8.00	6.93	0.0875	0.0071	12.3	———	———
$HCOOC_2H_5$	15.42	8.38	7.04	0.0901	0.0087	10.3	———	———
C_6H_6	15.17	7.81	7.36	0.0850	0.0074	11.5	———	———
C_2H_5OH	14.98	10.65	4.33	0.0768	0.0066	11.6	0.00269	28.2
CCl_4	16.09	8.00	8.09	0.0856	0.0076	11.3	———	———
$(C_2H_5)_2O$	16.09	6.90	9.19	0.0803	0.0097	8.3	0.00298	26.9
							———*	
Average				0.0877	0.00801	11.1	0.00311	28.1
Mean deviation				±7.4%		±10%		±4%

In general, the net heats of adsorption are, for the most part, of the same magnitude as the heats of vaporization. They vary from half as much for methyl alcohol to a half more for ether and propyl chloride. While the heats of vaporization of all liquids are less at 0° than at 25°, the net heats of adsorption are greater at 25° than at 0°. The one exception to this rule is ethyl chloride. This exception may be apparent, rather than real, since the calculation of h involved the calculation of the molecular volume of ethyl chloride as a liquid at 25°. The value of Q, the heat of vaporization, of ethyl chloride, may also be in error, since its value was obtained from existing vapor pressure data. Lamb and Coolidge report the heat of vaporization of benzene at 0° to be 7.81 K· cals. This value is much smaller than the values [21], 8.28 and 8.51, as given by Regnault and Young, respectively. The data obtained by these two investigators is given in Table XII for comparison.

The net heats of adsorption per 1 cc. of liquid on 10 g. of charcoal at 25°, (Col. 5), were obtained by dividing the net molecular heat of adsorption by the molecular volume of the liquid at 25°. It is evident that these net heats of adsorption per 1 cc. of liquid are all very nearly the same, the average deviation from the mean, 0.0969 K. cals., being only 7.1 percent. Except for ethyl chloride, these net heats per cc. are all higher than the corresponding values at 0° by about 10 percent. The mean deviation is practically the same at both temperatures. Such a small deviation led Lamb and Coolidge to believe that the net heats of adsorption must be due to the attractive forces of the charcoal, and that for a given amount of capillary space the heat liberated is identical, or nearly so, for all liquids.

Following the methods of our predecessors, we have calculated the heat of compression, in small calories, per atmosphere per cc. of liquid at atmospheric pressure. This calculation was made by the use of the relation:

$$\frac{dQ}{dT} = \left(\frac{dv}{dP}\right) : \frac{T}{42.7}$$

The values of $\frac{dv}{dT}$ were obtained by substituting the values of the temperature and the constants in the expression obtained by differentiating series formulae of the type: $v_t = v_0(1 + \alpha t + \beta t^2 + \gamma t^3)$, as given in the Landolt-Börnstein Tables. In every case the values are somewhat higher than the corresponding values at 0°. This seems highly significant, since it may afford an explanation why the heat of adsorption might not change with temperature. That is, the change in the heat of vaporization may be compensated by a corresponding change of opposite sign in the heat of compression.

The quotients of the net heats of adsorption divided by the heats of compression give us the attractive forces of the charcoal acting on the various liquids. These quotients are given in column 7 of Table XI. The average value of the attractive forces is about 10000 atmospheres. The comparison of these values with those obtained for 0° show clearly that these forces are diminished with rise in temperature, and in some cases markedly so. Because

[21] Landolt and Börnstein: "Tabellen."

of this high pressure, Lamb and Coolidge state that we are not justified in using heats of compression at 1 atmosphere in making these computations; that instead we should use the mean heats of compression obtained by integration over the whole pressure range covered. They have calculated the attractive forces of some of their vapors at 0° from the heats of compression computed by Bridgman[22] at pressures up to 12000 atmospheres. Five of our vapors were studied by Bridgman at 20°, 40°, 60° and 80°. The values of the heats of compression at 25° have been interpolated and are given in column 8. The average value is about 12 percent higher than at 0°; the individual values show an even greater constancy.

If we now divide the net heats of adsorption by these better values of the heats of compression, we obtain the attractive forces given in column 9. The average value of the attractive force of carbon for these five vapors is 29000 atmospheres, or about 3.1 percent higher than for the average of the seven studied at 0°. The rather considerable increase in the attractive force of carbon for methyl alcohol and ether is significant.

Whether or not the attractive force exerted by charcoal on all liquids is the same and independent of the temperature is still a question. We know relatively little regarding the conditions prevailing in liquids under high pressures. Furthermore, we know still less of the conditions existing when these liquids are under high pressures and at the same time in contact with the attractive forces of a powerful adsorbent. For example, Bridgman states that pure acetone solidifies at 20° when under a pressure of 8000 atmospheres. At what temperature would it solidify under this same pressure when in contact with porous charcoal? This we cannot answer.

Summary

1. A new calorimetric method has been devised by which it is possible to measure heats of adsorption at any temperature. It permits the use of temperatures at which the liquid phase is absent, and thus prevents the introduction of the thermal effect due to ordinary condensation.

2. The method possesses three important features. (a) Objectionable condensation effects are eliminated by having the calorimeter at the same temperature as that of the vapor to be adsorbed. (b) The charcoal bulb is of such a design that the heat evolved is quickly conducted outward to the calorimeter liquid. (c) The rise in temperature of a known weight of oil is read by a sensitive thermoelement.

3. The heats of adsorption of nine vapors on charcoal have been measured at 25°. The heat effects were found to be easily reproducible, and they are independent of the rate of adsorption of the vapor and of the previous history of the charcoal.

4. The heats of adsorption of these vapors are in close agreement with those obtained by Lamb and Coolidge for the same vapors at 0°.

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[22] Bridgman: Proc. Am. Acad., 49, 1 (1913).

ACKNOWLEDGMENT

The author wishes to express his grateful appreciation to Dr. J. N. Pearce, under whose direction and guidance the investigation was carried out. He also wishes to acknowledge his indebtedness to Mr. John Robbins, the glassblower, Mr. George Anderlik, the mechanician, and Mr. Garrett Thiessen, his colleague, for technical assistance.

JAN 20 1931
FEB 4 1931